Shaughnessy Number: <u>116001</u>

Date Out of EFGWB: <u>1/30/89</u>

TO: G. Werdig/B. Briscoe
Product Manager <u> 50 </u>
Registration Division (TS-767C)

FROM: Patrick Holden, Team Leader
Ground Water Team
Exposure Assessment Branch/EFGWB (TS-769C)

THRU: Henry Jacoby, Acting Chief
Exposure Assessment Branch/EFGWB (TS-769C)

Attached: please find the EFGWB review of:

Reg./File #: <u>   464569</u>

Chemical Name: <u>   TRICLOPYR</u>

Type Product: <u>   Herbicide</u>

Company Name: <u>   Dow Chemical Company</u>

Purpose: <u>Screen Soil Adsorption Study for Ground-Water DCI</u>

Date Received: <u> 8/31/88 </u>   Action Code: <u>   495</u>

Date Completed: <u> 1/24/89 </u>   EFGWB #(s): <u> 80996</u>

Monitoring Study Requested: <u> X </u>   Total Reviewing Time: <u>3.5 days</u>

Monitoring Study Volunteered: <u>   </u>

Deferrals to: <u>   </u> Ecological Effects Branch

                       <u>   </u> Dietary Effects Branch

                       <u>   </u> Toxicology Branch

1. <u>CHEMICAL</u>

   Chemical Name: 3,5,6-trichloro-2-pyridnyloxyacetic acid

   Common Name: Triclopyr

   Trade Names: Garlon, Crossbow, Grazon ET, Turflon

   Formulations:

   Chemical Structure:

2. <u>TEST MATERIAL</u>: Radiolabeled technical grade.

3. <u>STUDY ACTION/TYPE</u>: Soil adsorption/desorption study

4. <u>STUDY IDENTIFICATION</u>:

Woodburn, K.B.; Fontaine, D.D.; and Richards, J.F. 1988. A Soil
Adsorption/Desorption Study of Triclopyr. Laboratory Project ID
GHC-2017, Performed and submitted by Dow Chemical U.S.A.
(Agriculture Chemistry R&D Laboratories, MI). Accession Number
407498-01.

5. <u>REVIEWED BY</u>:

   Richard C. Doyle
   Chemist, GWTS
   EFGWB/EFED/OPP   Date: _____

6. <u>APPROVED BY</u>:

   Patrick W. Holden
   Chief, GWTS
   EFGWB/EFED/OPP   Date: _____

7. <u>CONCLUSIONS</u>:

      The triclopyr batch adsorption studies are acceptable and
partially fulfill EPA data requirements. The results demonstrate
that triclopyr is highly mobile in soil. Freundlich adsorption
coefficients (Kd) were 0.975 in Kalkaska sand, 0.571 in Londo
sandy loam, 0.165 in Commerce silt loam, and 0.733 in Mahoun clay
loam. There is no apparent correlation between Kd values and
either soil texture or organic carbon content. Therefore, Kd
values in heavy textured, high organic matter soils are expected

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to be low.

The desorption study with aged residues appears to be subject to significant errors, and, therefore, is not acceptable for fulfilling registration requirements. Despite the inaccuracies, the results of this study support the conclusions from the adsorption study. Triclopyr and its degradates appear to be highly mobile.

8. RECOMMENDATIONS:

Triclopyr is highly mobile. Additional data are needed to characterize the mobility of triclopyr degradates. Field testing (164-1) is needed to fully assess the potential for ground-water contamination.

9. BACKGROUND:

Triclopyr has been included in the ground-water data-call-in. The current submission is in response to this data call-in.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See DER.

11. COMPLETION OF ONE LINER:

To be completed.

12. CBI APPENDIX:

Not applicable.

CASE TRICLOPYR   STUDY   PM   50

CHEM

BRANCH: ENVIRONMENTAL FATE AND GROUND-WATER

FORMULATION 00 - ACTIVE INGREDIENT

Woodburn, K.B.; D.D. Fontaine; and J.F. Richards. 1988. A Soil
Adsorption/Desorption Study of Triclopyr. Project ID GHC-2017.
Performed and submitted by Dow Chemical U.S.A. Accession Number
407498-01.

DIRECT RVW TIME =   3 days

REVIEWED BY: R.C. DOYLE
TITLE: CHEMIST
ORG: EFGWB/EFED/OPP
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SIGNATURE:

CONCLUSIONS:

     The triclopyr batch adsorption studies are acceptable and
partially fulfill EPA data requirements (Subdivision N Guidelines
Section 162-1). The results demonstrate that triclopyr is highly
mobile in soil. Freundlich adsorption coefficients (Kd) were
0.975 in Kalkaska sand, 0.571 in Londo sandy loam, 0.165 in
Commerce silt loam, and 0.733 in Mahoun clay loam. There is no
apparent correlation between Kd values and either soil texture or
organic carbon content. Therefore, Kd values in heavy textured,
high organic matter soils are expected to be low.

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subject to significant errors, and, therefore, is not acceptable
for fulfilling registration requirements. Despite the
inaccuracies, the results of this study support the conclusions
from the adsorption study. Triclopyr and its degradates appear
to be highly mobile.

MATERIALS AND METHODS:

     The test materials used in this study were: #2 and/or #6

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ring-labeled ^{14}C-triclopyr (100% radiochemically pure, 11.24 m Ci/mole) dissolved in distilled water to yield 3.86×10^7 disintegrations per minute (DPM) per ml (400 ug/ml); analytical-grade triclopyr (99+% pure) dissolved in acetonitrile (2040 mg/l); and analytical-grade 3,5,6-trichloro-2-pyridinol (TCP) dissolved in acetonitrile 1980 mg/ml). Ad/desorption studies were conducted with four soils: Kalkaska sand, Commerce silt loam, Mahoun clay loam, and Londo sandy loam. Physical/chemical characteristics of these soils are given in Table 1. The soils were stored at 4°C prior to testing to preserve microbial activity.

Two analytical methodologies were used: liquid scintillation counting (LSC) and reverse phase high pressure liquid chromatography (HPLC). LSC was done using a Packard 4000 programmed for a single isotope, with 2-minute or 2 sigma time cutoff. Quench was determined by measuring the position of spectral index with the external standard. Reference ^{14}C standards were counted throughout the experiment to verify instrument calibration.

The HPLC analyses were run with a C_{18} column using a mixture of acetonitrile and water, each containing 1.0% acetic acid (U/V) and 0.5 ml/l of N,N-dimethyl-octylamine, as the mobile phase. Ratios of acetonitrile to water and rates of mobile phase flow were varied with time. Absorbance at 235 mm was used to detect elution. When radiolabeled compounds were analyzed eluate fractions were collected at 1-minute intervals and were analyzed for total ^{14}C-activity by LSC. A second set of gradient conditions for the mobile phase was used to verify the identity of TCP in the desorption soil samples.

Adsorption Kinetics Study

The Kalkaska sand soil (5 g) was shaken with 15 ml of ^{14}C-triclopyr in 0.01$\underline{N}$ aqueous $CaCl_2$ (14.94 mg/ml) for 48 hours (ambient temperature). After 1, 4, 20, 24, and 48 hours, the sample was centrifuged for 20 minutes, 200 ul of supernatant was removed, and the sample was then returned to the shaker. ^{14}C-activity in the 200 ul subsample was quantified using LSC.

Adsorption Study

^{14}C-Triclopyr was combined with non-radiolabeled triclopyr in 0.01$\underline{N}$ aqueous $CaCl_2$ to give four solutions (0.97, 4.96, 9.93, and 14.94 ug/ml) with a ^{14}C content of approximately 3.5×10^4 DPM/ml in each solution. Aliquots (15 ml) of each solution were shaken (48 hours @ ambient temperature) with 5-g (air-dried) portions of each of the four soils. All samples were run in duplication. After shaking, the samples were centrifuged, and the supernatant was separated from the soil. Control samples (no soil) were subjected to the same procedure (1 replicate of each concentration).

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Total radioactivity in the supernatant was quantified by LSC. HPLC radioassays were conducted on supernatant from the second replicate of each soil equilibrated with the highest concentration of triclopyr (14.94 ug/ml) (coded #4B in the submission). Solutions from the controls were also analyzed by HPLC with radioassay of the eluate.

The soils samples were air-dried (2 days @ ambient temperature), ground to a powder, and then combusted (triplicate 1-2 g samples). ^{14}C released as $^{14}CO_2$ was quantified by LSC. The The ^{14}C found in the soil was corrected for the solution-phase ^{14}C remaining in the soil pore water.

Average aqueous and adsorbed triclopyr concentrations were used to construct Freundlich adsorption isotherms for each soil. Linear regression was used to calculate a best fit curve. The adsorption Kd (adsorption coefficient) and n values were determined from the intercept and slope.

Aged Residues

Three soil aerobic metabolism flasks (two 250-ml Erlenmeyers connected via a sidearm) were set up for each of the four soils. One side of each metabolism flask contained 50 g of soil (at 75% of 1/3 bar moisture) that was treated with 100 ul of an aqueous ^{14}C-triclopyr solution (3.86 x 10^6 DPM/flask; 0.8 ug/g). The connected erlenmeyer in each metabolism flask contained 100 ml of 0.2$\underline{N}$ NaOH. The flasks were maintained at 25°C in the dark. After 0, 15, and 30 days, a single flask for each soil was frozen and the NaOH trap was assayed for ^{14}C-activity. ^{14}C remaining in the aged soil was quantified by combustion and LSC.

Desorption Kinetics of Aged Residues

An aliquot of the Kalkaska sand and the Londo sandy loam aged soils (4 g) was shaken with 15 ml of 0.01$\underline{N}$ CaCl$_2$ for 141 hours at ambient temperature (air temperatures of 24-25°C). After 1, 4, 21, 28, 45, 48, 72, and 141 hours, the samples were centrifuged (20 minutes), a 200-ul subsample of supernatant was removed, and the samples were then returned tot he shaker. Total ^{14}C in the 200 ul subsamples were quantified by LSC.

Extractability of Aged Residues

Ten grams of each triclopyr treated aged soil (0-, 15-, and 30-day of aging) were extracted (shaking overnight) with 15 ml of acetonitrile/1.5$\underline{M}$ H$_3$PO$_4$ (96:4) and 2 ml of 1.5$\underline{M}$ H$_3$PO$_4$. Centrifugation was used to separate the solid and liquid phases. The soil samples were extracted two more times by shaking for 1 hour with the acidified acetonitrile (15 ml acetonitrile/1.5$\underline{M}$ H$_3$PO$_4$ (95:4)). The combined extracts were brought up to 50 ml with acetonitrile. Subsamples were assayed by LSC to quantify ^{14}C-activity. HPLC analyses were performed to quantify the parent and its metabolites.

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The extracted soils were then extracted three times with 0.5N NaOH. The first extraction was by shaking overnight; subsequent extractions were by shaking for 1 hour. Extracts were combined, brought up to 50 ml with 0.5N NaOH, and analyzed by LSC to quantify the ^{14}C content.

Following organic and caustic extractions, the soil was air-dried, ground to a powder, and combusted. The ^{14}C released by combustion was quantified by LSC.

Desorption of Aged Residues

Four-gram subsamples of each aged soil were shaken with 15 ml of 0.01N CaCl$_2$ for 141 hours at 24-25°C, Following phase separation by centrifugation, the supernatant was analyzed for total ^{14}C-activity by LSC and for triclopyr and possible degradation products by HPLC. The soil was air-dried, ground to a powder, and combusted. [14]C released by combustion was quantified by LSC. Amounts of ^{14}C found in the soil were corrected for the radioactivity in the soil pore water.

Concentrations of triclopyr and TCP were used to calculate linear desorption coefficients (Kd). A Dow Chemical Company developed software package, SimuSolv, was used to describe the desorption data using the "two-compartment" model.

Storage Stability

A 50-g sample of Londo sandy loam (75% of 1/3 bar moisture) was spiked with 3.92 x 10^{6} DPM of ^{14}C-triclopyr. Ten grams of the soil was immediately extracted (acetonitrile/acid) and analyzed by HPLC radioassay. The remaining soil was stored at -20°C for 73 days before extraction and HPLC analysis.

RESULTS:

The adsorption of triclopyr on Kalkaska sand resulted in an initial rapid decline in the aqueous concentration. The rate of adsorption decreased with equilibration time. Adsorption after 24 hours was not evident (Table 2).

The adsorption data are summarized in Table 3. Coefficients of determination (r^2) (calculated by reviewer using individual data points) were $\geq$ 0.918 for three of the soils. The r^2 for the fourth soil, Kalkaska sand, was 0.712; however, the lack of fit is largely the result of the poor agreement between replicates at the 14.94 ug/ml concentration. Adsorption coefficients were low, ranging from 0.16 (Commerce silt loam) to 1.04 (Kalkaska sand). Recovery of ^{14}C from individual samples was 97.6 - 103% for all soils except the Kalkaska sand where recovery ranged from 85.4 to 99.2%.

The HPLC analysis of the supernatant from one replicate of the 14.94 ug/ml samples indicated that degradation of triclopyr during the 48-hour adsorption equilibration was negligible.

Table 4 summarizes the distribution of ^{14}C in ^{14}C-triclopyr treated soils after 0-30 days of aging. The evolution of ^{14}C as $^{14}CO_2$ varied substantially with soil, 5.1% from Kalkaska sand to 28.3% from the Mahoun clay loam after 30 days incubation. The extractability of triclopyr was high (103 - 112% at day -0) except for the Mahoun clay loam where only 54% of the ^{14}C was found in the acidified acetonitrile extract. The accumulation of ^{14}C in bound residue (^{14}C found in soil following the acidified acetonitrile extraction, i.e., the NaOH extract and post extraction combustion) was low (4.1 - 9.1% after 30 days) for all soils except the Mahoun clay loam where the bound residue comprised 23.4% of the total ^{14}C. The mass balance calculated from the $^{14}CO_2$ evolution and the pre-extraction combustion ranged from 80.2 to 94.1%. The mass balance when calculated from the $^{14}CO_2$ evolution; acetonitrile and NaOH extractions, and the post-extraction combustion ranged from 60.3 to 113.0% (reviewer calculated).

The parent and TCP were the only ^{14}C-products that were identified in the organic extract of the aged soils and in the $CaCl_2$ solution following desorption. The relative amounts of TCP and triclopyr are given in Table 5. Triclopyr and TCP accounted for the majority of ^{14}C eluted from the HPLC, >95% in most cases. The largest quantity of unidentified ^{14}C was 13.75% (30-day Mahoun clay loam).

The results of the desorption study are summarized in Tables 6 and 7. The percentage of ^{14}C as triclopyr or TCP (as determined by HPLC) was multiplied times the total ^{14}C-activity found in the $CaCl_2$ desorption solutions to determine the concentration of each of these compounds. Similarly, the percentage of ^{14}C found as triclopyr or TCP found from the HPLC analyses of the acetonitrile extracts of the soils was multiplied by the total ^{14}C in each soil sample (combustion) to determine soil concentrations. Desorption coefficients (Kd) were calculated from the ratio of concentration of test material in soil to the concentration in solution.

The results of the kinetics study for desorption of aged residues are given in Table 8. The 0-day samples were reported to reach equilibrium within 24 hours. Equilibrium in the 15- and 30-day samples was reported to occur between 24 and 72 hours.

AUTHOR'S CONCLUSIONS

Adsorption of ^{14}C-triclopyr apparently reached equilibrium after 24 hours of shaking. Therefore, 48 hours was selected as the equilibration time for the adsorption study. An average Koc of 59 from the adsorption study indicates potential for triclopyr mobility in soil if precipitation occurs immediately following

application.   The mass balance was excellent, averaging > 90% for each soil.

The metabolism of ^{14}C-triclopyr during soil aging was evident.   Degradation produced ^{14}C-TCP as an intermediate and ^{14}CO$_2$.   TCP concentration increased with incubation time. However, TCP is only a transient intermediate which in turn is degraded to yield CO_2.   The overall recovery of ^{14}C from the aged soils was excellent: 88% average recovery if using pre-extraction combustion data, 94.4% if using extraction/post-extraction combustion data.   Total recovery for the 30-day samples was somewhat erratic, especially for the Mahoun clay loam.   It is believed that the blocky, well-aggregated structure of this soil contributed to a non-uniform application of radiolabeled test material, which resulted in inconsistent recoveries.

Quantities of TCP produced were too small to permit positive identification by gas chromatography/mass spectrometry.   However, the HPLC results from using two mobile phase gradients were in very good agreement, strongly indicating that TCP was the sole intermediate metabolite.   The relative amounts of TCP found in the organic extracts and in the $CaCl_2$ desorption solutions demonstrate that TCP is more readily extracted into 0.01$\underline{N}$ $CaCl_2$ than into acetonitrile/acid.

The desorption Kd and Koc values increased (approximately 2-3 fold) on all soils from day 0 to day 15 with generally only a slight increase in Kd and Koc observed from day 15 to day 30. The data indicate that the leaching potential of triclopyr should decrease significantly as it ages on the soil.   This time dependent decrease in mobility may be attributed to the diffusion of triclopyr into inaccessible pores of soil aggregates.

The kinetics of this time dependency was evaluated using the "two-compartment" model as shown in the following equation, where B is the test compound

$$ B \underset{K_1}{\overset{K_0}{\rightleftharpoons}} A \underset{K_3}{\overset{K_2}{\rightleftharpoons}} U $$
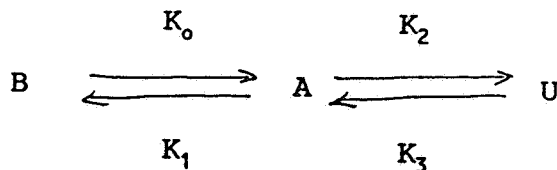
in the bulk aqueous solution, A is the available sorbed material, and U denotes the unavailable sorbed solute.   Rate constants at equilibrium conditions were estimated by solving a series of differential equations which describe the rates of transfer between bulk solution, available sorbed, and unavailable sorbed material.   A desorption Kd was then calculated from these rates. The calculated Kd (2.4) for the 15-day Kalkaska soil was nearly identical to the experimentally determined Kd (2.31).   The model fit the experimental data quite well (Figure 1), and it appeared

that the "two-compartment" model successfully simulated the desorption behavior of triclopyr. The model indicated that during desorption the transfer of available sorbed triclopyr to the unavailable pool was negligible. After 141 hours of shaking, 98% of the sorbed triclopyr was predicted to be in the available pool. the successful application of the "two-compartment" model to the desorption data and the increases in adsorption Koc values as triclopyr is aged in soil indicate the gradual movement of the surficial triclopyr into the soil matrix. Results from this study indicate that the leachability of triclopyr may decrease substantially as the residence time in soil increases.

Desorption Koc values for TCP were low (average Koc for 30-day samples of 3 soils and 15-day samples of Mahoun soil was 42), which indicates potential mobility in the soil profile.

HPLC analyses of triclopyr treated soil after 73 days storage (frozen) indicated that degradation of triclopyr did not occur (extracted material was 97% pure).

REVIEWER'S DISCUSSION

The adsorption data are adequate to demonstrate that triclopyr is highly mobile in the four soils tested. The data conform to the Freundlich model and reported Kd values range from 0.165 to 0.975. The solid-phase versus liquid-phase relationship is not linear, 1/n values were 0.481-0.806.

A number of minor errors were noted. Averaged data was used to calculate Freundlich value. Individual data pairs should have been entered, but the magnitude of the error is insignificant. The Freundlich equation was incorrectly reported. The natural log (ln) was reported instead of log base 10, and the 1/n value was reported as N. However, the Freundlich values reported were calculated using the base 10 log. The Koc calculations were performed using organic carbon contents. This was recalculated by the reviewer; the Kd values were normalized to the organic matter (Kd/(% or C x 1.72)). The specific activity of the test material was incorrectly reported in the text, but correctly reported in sample calculations. These errors are either inconsequential or have been corrected by the reviewer.

A somewhat potentially more serious problem is inaccuracy associated with the radioassay techniques. Inconsistencies and erratic recoveries of ^{14}C from the desorption study suggest that problems in combustion and/or LSC operations may have influenced the adsorption data. However, additional data needed to evaluate this potential error are not requested, given the magnitude of the potential error and the very low adsorption Kd values. It is clear that triclopyr is very mobile and minor adjustment to improve the accuracy of the Kd values will not change this assessment.

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Significant error is associated with the desorption study. Therefore, the results of this study will not fulfill data requirements. The desorption study was run at only one concentration. This concentration (equivalent to 4 lb ai/acre) was too low. But, more importantly, the Kd values calculated from these data assume a linear relationship between the solid-phase and solution-phase triclopyr which is not a valid assumption. The adsorption data demonstrated that this relationship is not linear.

As already noted, the submitted data has inconsistencies which indicated poor accuracy with at least some of the radioassay procedures. Given this error and the apparent low production of TCP during soil aging, the TCP desorption data is potentially too inaccurate to use.

The determination of TCP and triclopyr concentrations in soil after desorption was based on the total ^{14}C remaining in the soil and the relative amounts of TCP and triclopyr found in the acetonitrile extract. These data are highly questionable because the extraction efficiency for TCP and triclopyr were not reported. Available data suggest that the acetonitrile extraction is not very efficient in extracting TCP from soil.

The storage stability data reported did not provide any information on the recovery of triclopyr after frozen storage.

Table 1. PHYSICO-CHEMICAL PROPERTIES OF SOILS USED IN ADSORPTION/DESORPTION EXPERIMENTS

Soil Series	Soil Type	% Org. Carbon	% Sand	% Silt	% Clay	Soil pH	C.E.C.[a]	% Moisture 1/3 bar	Air Dry	Oven Dry Weight(g)[b]
Kalkaska	Sand	0.73[c]	88	8	4	5.0	2.0	7.18	0.61	49.70
Commerce	Silt loam	0.67	34	52	14	7.7	9.7	20.17%	1.01	49.50
Mahoun	Clay loam	1.38	23	41	35	6.6	8.5	31.70%	7.00	46.73
Londo	Sandy loam	2.25	70	20	10	7.5	18.2	13.54%	0.78	49.61

[a] Cation Exchange Capacity (meq/100 g)

[b] Oven Dry Weight for a 50-g soil sample at air-dry content.

$$\text{Oven Dry Weight (g)} = \frac{\text{Wet Weight (50 g)}}{1 + (\% \text{ Air Dry Moist}/100)}$$

[c] Value determined in GH-C 1873; unpublished data of The Dow Chemical Company.

Table 2.   ADSORPTION KINETICS FOR TRICLOPYR STANDARD #4A ON KALKASKA SAND SHAKEN AT LOW SPEED
FOR 48 HOURS ON A HORIZONTAL SHAKER

Time (Hr)	Average DPM/mL[a]	Standard Deviation DPM/mL[a]
1	30644	471
4	29934	457
20	29192	270
24	28690	7
48	28893	65

[a] Aqueous phase samples were taken as duplicate 200 uL aliquots. Each aliquot was counted three times and averaged; the duplicates were then averaged and the standard deviation determined.

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Table 3. ADSORPTION Kd AND Koc VALUES FOR TRICLOPYR ON FOUR SOILS. THE ADSORPTION Kd VALUES
WERE CALCULATED USING SIMPLE REGRESSION ANALYSIS AND THE LINEARIZED FREUNDLICH
EQUATION: LOG (SOIL [ug/g]) = LOG Kd + (1/n)*LOG (SOL'N [ug/ml])[a]

Soil	Coefficient of Determination ($r2$)	$1/n$[b]	Kd (ml/g)	Koc[c] (ml/g)
Kalkaska sand	0.998	0.806	0.975	78
Londo sandy loam	0.954	0.603	0.571	15
Commerce silt loam	0.932	0.481	0.165	15
Mahoun clay loam	0.986	0.622	0.733	31

[a] The equation was reported as ln (Soil [ug/g]) = ln Kd + N * ln (Sol'n [ug/ml]).
Average values were used for the regression, not individual data points.

[b] Reported as N.

[c] Calculated by reviewer.

Table 4.   DISTRIBUTION OF ^{14}C IN ^{14}C-TRICLOPYR TREATED SOIL AFTER 0, 15, AND 30 DAYS OF AGING

Soil	Aging (days)	Pre-extraction Combustion	$^{14}CO_2$	Organic Extract	NaOH Extract	Post-extraction Combustion	Mass Balance[a] A	B
Kalkaska sand	0	86.2	--	112.4	--	0.6	86.2	113.0
	15	86.4	0.2	104.9	1.9	0.1	86.7	107.1
	30	83.8	5.1	76.9	2.3	0.8	88.9	85.1
Londo sandy loam	0	86.5	--	104.8	--	2.2	86.5	107.0
	15	83.9	1.2	102.0	2.0	1.8	85.1	107.0
	30	69.8	10.4	98.0	1.5	2.6	80.2	112.5
Commerce silt loam	0	90.3	--	102.7	--	2.8	90.3	105.5
	15	85.0	9.1	106.0	5.5	1.0	94.1	121.6
	30	75.4	9.3	65.8	5.1	4.0	84.7	84.2
Mahoun clay loam	0	93.4	--	54.3	--	6.0	93.4	60.3
	15	78.6	10.4	90.6	1.1	3.5	89.0	105.6
	30	60.0	28.3	46.0	12.1	11.3	88.3	97.7

[a]   The A column is the total from the pre-extraction combustion and $^{14}CO_2$.   The B column (calculated by reviewer) is the total of $^{14}CO_2$, organic extract, NaOH extract, and the post-extraction combustion.

Table 5. PERCENT COMPOSITION OF TRICLOPYR AND PYRIDINOL IN ACETONITRILE AND AQUEOUS (0.01N $CaCl_2$) EXTRACTS, BY HPLC RADIOASSAY

SOIL	% TRICLOPYR Acn Ext[a]	% TRICLOPYR $CaCl_2$ Ext[a]	% PYRIDINOL Acn Ext[b]	% PYRIDINOL $CaCl_2$ Ext[b]
O DAY				
P42	100.00	99.36	– – – –	– – – –
M189	100.00	99.95	– – – –	– – – –
M191	100.00	99.92	– – – –	– – – –
M209	100.00	99.94	– – – –	– – – –
15 DAY				
P42	96.54	99.97	1.24	– – – –
M189	100.00	99.43	– – – –	0.06
M191	99.98	98.04	– – – –	1.48
M209	98.27	96.29	0.35	3.19
30 DAY				
P42	95.75	84.36	1.00	12.24
M189	99.19	95.92	0.60	3.50
M191	96.60	96.51	2.00	3.43
M209	85.64	98.70	0.61	– – – –

[a] %Triclopyr in acetonitrile and $CaCl_2$ extracts was determined by HPLC analysis; retention time of 42-43 minutes.

[b] %Pyridol in acetonitrile and $CaCl_2$ extracts was determined by HPLC analysis; retention time of 20-23 minutes.

Table 6. TRICLOPYR CONCENTRATION IN SOIL AND AQUEOUS PHASE FOLLOWING SOIL/WATER DESORPTION EQUILIBRATION; THE RESULTANT DESORPTION K_d AND K_{oc} VALUES ARE CALCULATED.

Soil	Days Incubated	Aqueous (DPM/mL)[a]	Aqueous (ug/mL)[b]	Soil (DPM/g)[c]	Soil (ug/g)[d]	K_d(lin) (mL/g)[e]	K_{oc} (mL/g)[f]
Kalkaska Sand	0	12460	0.128	14614	0.150	1.17	94
	15	9962	0.102	23028	0.237	2.31	184
	30	8550	0.088	21413	0.220	2.50	199
Londo Sandy Loam	0	13396	0.138	9563	0.098	0.71	19
	15	11020	0.113	18332	0.188	1.67	43
	30	10422	0.107	20359	0.209	1.95	51
Commerce Silt Loam	0	15343	0.158	5268	0.054	0.34	30
	15	12500	0.129	10911	0.112	0.87	76
	30	12125	0.125	11565	0.119	0.95	83
Mahoun Clay Loam	0	10584	0.109	14841	0.153	1.40	59
	15	4617	0.048	24486	0.252	5.30	223
	30	4974	0.051	22544	0.232	4.53	191

Average 0-Day K_{oc} = 87 mL/g (Stnd. Dev. = 58)
Average 15-Day K_{oc} = 226 mL/g (Stnd. Dev. = 148)
Average 30-Day K_{oc} = 225 mL/g (Stnd. Dev. = 130)

[a] Aqueous phase samples were taken as duplicate 200 uL aliquots. Each aliquot was counted three times on the LSC and averaged; the duplicates were then averaged and modified for triclopyr content.

[b] Calculated ug/mL from "Aqueous DPM/mL" value and specific activity of 11.24 uCi/umole.

[c] The soil phase was analyzed by triplicate combustions of the dried, desorbed soil samples. The combustion DPM/g values were then corrected for DPM in the soil pore water, averaged, and modified for triclopyr content in the soil extract HPLC assay.

[d] Calculated ug/g from "Soil DPM/g" value and specific activity of 11.24 uCi/umole.

Table 6. (continued)

[e] The Kd (lin) represents the ratio of soil (DPM/g)/aqueous (DPM/ml).

[f] Calculated by reviewer.

Table 7. 3,5,6-TRICHLORO-2-PYRIDINOL (TCP) CONCENTRATION IN SOIL AND AQUEOUS PHASE
FOLLOWING SOIL/WATER DESORPTION EQUILIBRATION; THE RESULTANT DESORPTION
K_d AND K_{oc} VALUES ARE CALCULATED

Soil	Days Incubated	Aqueous (DPM/mL)[a]	Aqueous (ug/mL)[b]	Soil (DPM/g)[c]	Soil (ug/g)[d]	K_d(lin) (mL/g)	K_{oc} (mL/g)[e]
Kalkaska Sand	30	1241	0.0100	229	0.0018	0.18	15
Londo Sandy Loam	30	380	0.0030	123	0.0010	0.33	8
Commerce Silt Loam	30	416	0.0033	239	0.0019	0.58	50
Mahoun Clay Loam	15	153	0.0012	87	0.0007	0.58	24

Average Desorption K_{oc} = 42 mL/g (Stnd. Dev. = 32)

[a] Aqueous phase samples were taken as duplicate 200 uL aliquots. Each aliquot was counted three times on the LSC and averaged; the duplicates were then averaged and modified for TCP content.

[b] Calculated ug/mL from "Aqueous DPM/mL" value and specific activity of 11.24 uCi/umole.

[c] The soil phase was analyzed by triplicate combustions of the dried, desorbed soil samples. The combustion DPM/g values were then corrected for DPM in the soil pore water, averaged, and modified for TCP content in the soil extract HPLC assay.

[d] Calculated ug/g from "Soil DPM/g" value and specific activity of 11.24 uCi/umole.

[e] Calculated by reviewer.

TABLE 8.   DESORPTION KINETICS FOR TRICLOPYR ON TWO SOILS SHAKEN AT LOW SPEED
            FOR 141 HOURS ON A HORIZONTAL SHAKER

Soil	# Days Incubated	Average DPM/mL[a] Shaking Time (Hours)								
		1	4	21	24	28	45	48	72	141
Kalkaska[b] Sand	0	11510	12965	13460	13330	13285	13320	13205	12800	12545
	15	5375	6375	7870	8105	8020	8345	8780	9430	9965
	30	5845	7005	------------Sample Broken-------------------------------						
Londo Sandy Loam	0	12865	14125	14270	14020	14185	14100	14160	14165	13395
	15	8340	9240	10185	10175	10390	10420	10475	10720	11025
	30	8695	9540	10740	10560	10720	10675	10555	10670	10865

[a] Aqueous phase samples were taken as duplicate 200 uL aliquots. Each aliquot was counted three times and averaged; the duplicates were then averaged and presented as DPM/mL.

[b] Individual four gram soil samples (4 g) were shaken with 15 mL of 0.01N $CaCl_2$ for the times indicated. At each sampling time, the sample was removed, centrifuged, and aliquots taken of the aqueous phase for analysis.